



Full Length Article

RE (La, Nd and Yb) doped CeO₂ abrasive particles for chemical mechanical polishing of dielectric materials: Experimental and computational analysisJie Cheng^{a,b}, Shuo Huang^c, Yang Li^d, Tongqing Wang^a, Lile Xie^a, Xinchun Lu^{a,*}^a State Key Lab of Tribology, Tsinghua University, Beijing 100084, China^b Laser Micro/Nano Fabrication Laboratory, School of Mechanical and Vehicular Engineering, Beijing Institute of Technology, Beijing 100081, China^c Applied Materials Physics, Department of Materials Science and Engineering, Royal Institute of Technology, Stockholm SE-100 44, Sweden^d Department of Chemistry, Tsinghua University, Beijing 100084, China

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ABSTRACT

Ce³⁺ in CeO₂, rather than Ce⁴⁺, is believed to provide assistance to the breaking up of Si–O bond during chemical mechanical polishing (CMP) of silica. In the paper, lanthanide metals (La, Nd and Yb) doped CeO₂ nanoparticles were synthesized by modified incipient impregnation method in order to improve the content of Ce³⁺ in CeO₂ as polishing. X-ray photoelectron spectroscopy (XPS) experiments and density function theory (DFT) calculation demonstrate this approach could achieve surface doping of CeO₂ nanoparticles, and facilitates the formation of oxygen vacancy and Ce³⁺ content. CMP experiments show that the polishing rate and the surface quality of silica wafer are obviously improved by using the doped CeO₂ as abrasive particles. Especially for Nd/CeO₂, content of Ce³⁺ increases from 0.146 to 0.235, the polishing rate of silica is accelerated by 29.6% in alkaline slurries, and a better surface quality (Sa = 9.6 Å) is obtained.

1. Introduction

Chemical mechanical planarization (CMP) is the enabling technology mainly applied to achieve both local and global planarity of semiconductor devices. Continuous technology advances have led to an increasing importance of CMP technique. The new device architectures and the relevant scaling challenges result in strict tolerance in defectivity, the non-uniformity and the material removal variation during CMP so as to meet performance and yield targets. Ceria (CeO₂), as one of the most widely used abrasive particle in CMP slurry, has gained wide application in the traditional dielectric polishing processes of integrated circuit (IC), such as the CMP of shallow trench isolation (STI) and inter-level dielectric (ILD) [1,2]. The ceria based-slurry is often capable of achieving a high ratio of oxide (e.g. SiO₂) material removal rate to nitride (e.g. Si₃N₄) removal, which is important to minimize the nitride loss in the crucial region in STI [3,4]. Apart from this, the ceria-based slurry could obtain a high removal efficiency of dielectric at a low dosage in slurry (≤1 wt%), while for colloidal SiO₂ abrasives the dosage could be ≥10 wt% to achieve identical material removal rate (MRR) [5–7]. Emerging technologies such as fin field-effect transistor (FinFET) have proposed more rigorous control for the CMP of dielectrics. Under this condition, ceria, as the most applicable abrasive particle, gains continuous emphasis on improving its performance in

the CMP of dielectric materials.

CeO₂ abrasives could realize the material removal of dielectrics under the effect of both mechanical abrasion and chemical reaction on the surface layer. It is widely believed that CeO₂ has a great affinity toward the silicon oxide, which helps in breaking the bonds on SiO₂ surface. The surface of SiO₂ in water is terminated with Si–OH while that of CeO₂ is Ce–OH. After the proton abstraction of Si–OH, Si–O[−] will react with Ce–OH to form Si–O–Ce bonds. Since the Si–O–Ce bonds are stronger than Si–O–Si bonds, the surface layer of SiO₂ is removed by the coupling of mechanical and chemical phenomena [3,8,9]. With regard to Si₃N₄, the material removal mechanism is similar, but more complex [10,11]. The actual MRR of dielectric materials depends on not only the additives in the slurry [4], but also the pH values of the slurry [1] and the characteristics of the CeO₂ particles, which will notably affect the physicochemical properties between the CeO₂ particle and the dielectric material surface [12–14]. Therefore, one way is to improve the CMP performance of dielectrics is to achieve surface modification of CeO₂ abrasive particles. Common methods include grafting functional groups to CeO₂ surface and synthesizing CeO₂-X core-shell composite particles [6,14–16].

Cerium has unique valence transition properties. In CeO₂ lattice, there is coexistence of Ce³⁺ and Ce⁴⁺ oxidation states and presence of intrinsic oxygen vacancies [17]. It has been proposed that Ce³⁺, instead

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of Ce^{4+} in CeO_2 abrasive particles, provides assistance to the breaking up of Si–O bond during CMP, leading to a high removal rate of silica [1,18,19]. Approaches to improve Ce^{3+} content in CeO_2 include reducing the particle size [20], lowering the CeO_2 content in polishing slurry [18], and introduction of dopants [21,22]. Trivalent dopants, mainly the rare-earth elements, could substitute Ce^{4+} , release more oxygen vacancies and cause partial reduction of neighboring Ce^{4+} to Ce^{3+} [23,24]. It has been reported that lanthanum impurities have been found on commercial CeO_2 abrasive particles [25]. Some lanthanide elements have been successfully used as the dopants in CeO_2 nanoparticles for catalytic applications and oxygen sensors [21,26,27].

Inspired by this idea, we proposed a new strategy to increase the Ce^{3+} fraction on the surface of CeO_2 nanoparticles, so as to improve the polishing rate of silica when CeO_2 was used as abrasive. Typical lanthanide elements RE (RE = lanthanum-La, neodymium-Nd and ytterbium-Yb) were chosen as the dopants. RE doped CeO_2 nanoparticles (marked as RE/ CeO_2) were prepared by modified incipient impregnation method, which was ideal to realize surface doping with fixed dopant load, and not change the original crystal structure of CeO_2 . The concentration of Ce^{3+} in CeO_2 was calculated by X-ray photoelectron spectroscopy (XPS) experiments and verified by first-principles calculation based on density functional theory (DFT). The polishing effects of silica using RE/ CeO_2 as abrasives were verified by CMP experiments. The findings in the manuscript provide a novel approach to improve polishing rate of silica in CMP application when CeO_2 is used as nano-abrasive particles.

2. Experimental and methods

2.1. Preparation of lanthanide elements doped CeO_2 nanoparticles

CeO_2 nanoparticles (99.95% in purity), with primary diameter less than 50 nm, was purchased from Sigma-Aldrich Corporation. Lanthanide nitrates were used as precursors: $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%) and $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (99.9%) from Aladdin Bio-Chem Technology Co. and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.9%) from MACKLIN Biochemical Co.. The process of the preparation of RE/ CeO_2 nanoparticles by modified incipient impregnation method is shown in Fig. 1. The impregnation volume of CeO_2 was measured to be 0.280 g/1 g. The load of dopant was set to be 5% in this paper. As a typical procedure, 5 g of the pristine CeO_2 was impregnated with the nitrate solution at the desired mass ratio. Then they were fully mixed to get a uniform paste. After aging for 12 h and drying at 120 °C for 12 h, the paste was calcined in muffle furnace at a heating rate of 5 °C/min, maintained at 400 °C for 2 h and then naturally cooled down to room temperature. Subsequently, the doped CeO_2 powders were ground in agate mortar. The calcination temperature was determined by the decomposition temperatures of nitrates which were measured by a thermo-gravimetric apparatus (TGA/DSC1, Mettler Toledo), with a heating rate of 10 °C/min. The prepared sample was denoted as RE/ CeO_2 (RE = La, Nd and Yb).

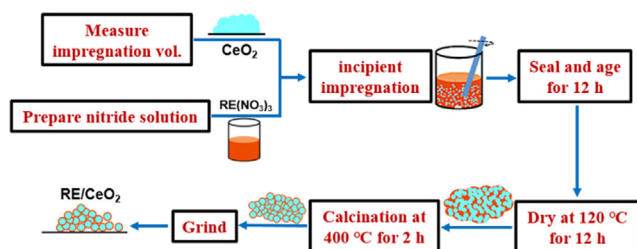


Fig. 1. Flow chart of the preparation of RE/ CeO_2 by improved incipient impregnation method. RE = La, Nd or Yb. Doping load is 5%.

2.2. Characterization of RE/ CeO_2 nanoparticles

The lattice structure of CeO_2 particles was measured by X-ray diffraction spectroscopy (XRD, D8ADVANCE, Bruker). Data were processed by Jade 5.0 software. The particle morphology and element distribution were characterized using transmission electron microscopy (TEM, JEM-2010F, JEOL) equipped with energy dispersive spectroscopy (EDS) system. The valence states of Cerium ($\text{Ce}^{3+}/\text{Ce}^{4+}$) were characterized using X-ray photoelectron spectroscopy (XPS, PHI Quantera II, Ulvac-Phi). The fraction of Ce^{3+} was calculated based on the deconvolution of Ce 3d spin-orbit doublet using XPSPEAK software.

The zeta potential of pristine CeO_2 nanoparticles was measured by a laser zeta potential analyzer (Nano ZS90, Malvern). The Zeta potential of PECVD silica thin film surface was measured by a surface charge analysis (SurPASS 3, Anton Parr). CMP experiments were carried out by polishing a 2 in. SiO_2 blanket wafer made by plasma enhanced chemical vapor deposition, on a CMP machine (Universal-150, Tianjin Hwatsing Technology Co.). The head/platen rotational speed was 100/100 rpm, the slurry flow rate was 100 ml/min, and the down pressure was 2 psi. The polishing time was 1.5 min and before each polishing an *ex-situ* conditioning of the pad was carried out for 30 s. The pad used was Politex from Dow Chemical Co.. The MRR of SiO_2 was calculated by measuring the film thickness (Resmap, Creative Design Engineering). In the measurement, the edge exclusion was 5 mm and 81 dots were measured within the wafer. The topography of polished SiO_2 surface was measured by a surface profilometer (Talysurf PGI, Taylor-hobson).

2.3. Ab initio calculations

The density functional calculations were carried out with the Vienna ab initio simulation package (VASP) [28,29]. The electron wave functions were described with the projector augmented wave (PAW) method [30]. Plane waves were included up to an energetic cut off of 500 eV. The exchange-correlation effects were treated with the generalized gradient approximation (GGA) in the form of Perdew, Burke and Ernzerhof (PBE) [31]. The effective Hubbard parameter U was employed to account for the strong on-site Coulomb repulsion amongst the localized 4f orbital for the lanthanide series elements [32]. In this study, $U = 5$ eV was applied to the 4f states of Ce and dopants, and in addition, $U = 5.5$ eV was applied to the 2p states of O [33]. A $2 \times 2 \times 2$ supercell of the cubic fluorite structure with 96 atoms was used as initial structural model. The Brillouin zone integrations were performed with a $2 \times 2 \times 2$ Monkhorst-Pack grid [34]. The structure optimizations were pursued until the force on each atom was less than 0.02 eV/Å. The equilibrium volume was extracted from the Birch–Murnaghane equation of state fitted to the ab initio total energies for different volumes.

3. Results and discussions

3.1. RE-doped (RE = La, Nd or Yb) CeO_2 by incipient impregnation method

The results of thermogravimetry experiments are shown in Fig. 2, which could be used to determine the calcination temperature of doped CeO_2 prepared by incipient impregnation method. The weight loss curves (TG) and derivative weight loss curves (DTG) refer to left Y axis and right Y axis, respectively. To avoid the influence of carrier and doping load on the decomposition temperature, nitride impregnated CeO_2 nanoparticles, instead of nitrates powder, were used as the samples [35]. In the DTG curves, the peak within lower temperature range (≤ 100 °C) indicates the loss of crystal water. The peaks at higher temperature range indicate the decomposition of nitrates. The decomposition temperature of $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ is comparatively lower at ca. 160 °C, and that for $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ is at ca. 400 °C. Therefore, the calcination temperature of nitrates impregnated CeO_2 was set at 400 °C, to ensure the thorough decomposition of nitrates and

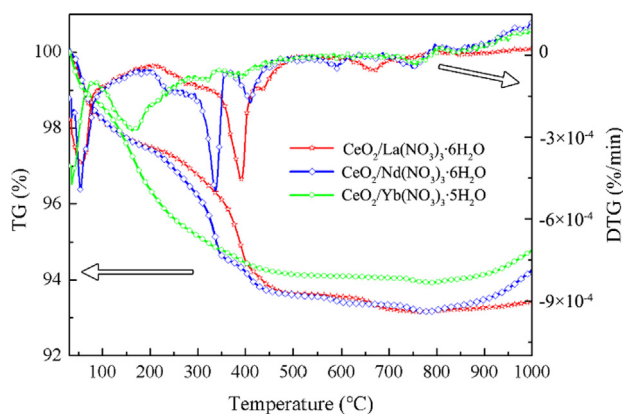


Fig. 2. Thermogravimetry (TG-DTG) curves of the $\text{RE}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ impregnated CeO_2 . RE = La, Nd or Yb. RE load is 5%.

to avoid further growth/agglomeration of the CeO_2 nanoparticles.

Fig. 3(a) and (b) shows the crystalline phase information of the prepared RE/CeO_2 particles (RE = La, Nd or Yb) by XRD. For comparison, the XRD patterns of lanthanide oxides prepared by direct calcination from lanthanide nitrides at the same temperature (400°C) are shown in Fig. 3(c). The XRD patterns of doped CeO_2 particles remain typical pattern of fluorite structure and correspond well with the standard data of JCPDS No. 65-5923 [36]. However the lanthanide oxides are almost amorphous. Thus, it is safe to say that the doping process does not introduce a secondary phase and the RE/CeO_2 particles remain the intrinsic lattice structure of CeO_2 . The only change observed after doping is the sharpening and weakening of the diffraction peaks, which is caused by the increase of lattice imperfections under the introduction of dopants, as is clearly shown in Fig. 2(b). According to the Debye-Scherrer equation [37], the grain size could be calculated based on the broadening of the diffraction peak and the Bragg angle. The calculated average particle size based on three main crystallographic plane (1 1 1), (2 2 0) and (3 1 1) is shown in Table 1. The doping process does not cause growth of the grain size, with a uniform diameter of ca. 20 nm. Due to the lattice distortion under the introduction of dopants, the lattice constant of RE/CeO_2 increases compared with pristine CeO_2 (Table 1), which can be directly correlated with crystal radii of dopants. The crystal radii (with 8 ligands) of La^{3+} , Nd^{3+} and Yb^{3+} are 1.29 nm, 1.24 nm and 1.13 nm, respectively [38], and all of them are larger than that of Ce^{4+} (0.97 nm) [39]. Therefore, the introduction of dopants will cause slight lattice expansion of CeO_2 . It is worth mentioning that the lattice constant is also affected by the content of Ce^{3+} (with the crystal radius of 1.27 nm), which will be discussed hereinafter.

The TEM and EDS mapping images of the RE/CeO_2 nanoparticles are shown in Fig. 4, which provide information of particle morphology and the element distribution. The shape of the RE/CeO_2 particle is near-spherical, and the doping elements uniformly distribute on the RE/CeO_2 nanoparticles, indicating that the doping is uniform without formation of secondary phases, coinciding well with the XRD results. The element distribution across single particle, with Yb/CeO_2 particle as an example, is shown in Fig. 5. In Fig. 5(b), the element intensities along Y axis were normalized for better clarity. It is noticeable that there are “teeth like” sharps on the curve of Yb element, which appear at the boundary of the nanoparticle. The appearance of the sharps indicates that the dopant element (Yb) concentrates at the surface of CeO_2 , instead of diffuses into the bulk of the particle. Therefore, it is safe to say that the doping method applied in this study could effectively achieve uniform surface doping on the CeO_2 nanoparticles.

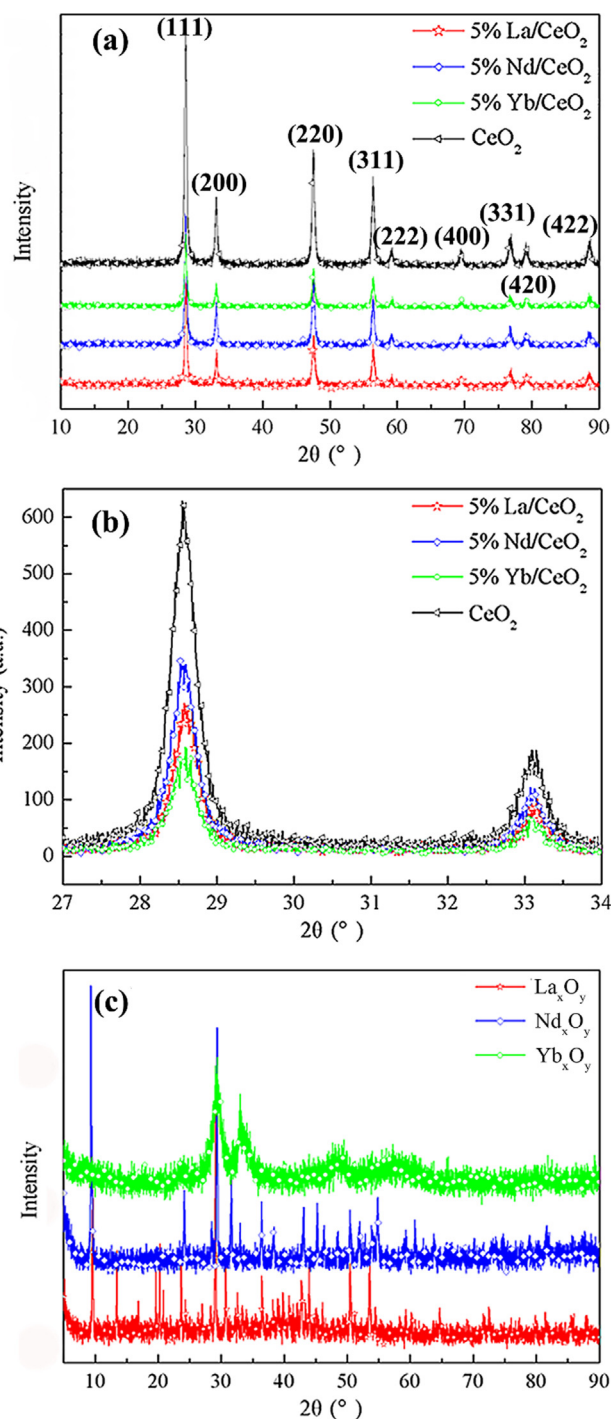


Fig. 3. XRD patterns of (a) RE/CeO_2 ; (b) enlarged drawing of (1 1 1) and (2 0 0) crystallographic planes in (a); (c) as calcined lanthanide metal oxides.

3.2. Influence of doping on oxygen vacancy and $\text{Ce}^{3+}/\text{Ce}^{4+}$ content

Fig. 6 shows the atomic structures and the electronic density of states (DOS) of the CeO_2 with and without defects, respectively. For the pristine CeO_2 , the highest occupied valance band is mainly determined by the O 2p states, with some contributions from the Ce 4f and 5d states, whereas the characteristic narrow peak above the Fermi level primarily consists of the Ce 4f states. The width of O 2p states is ~ 4.0 eV, and the energy gap between O 2p states and Ce 4f states is ~ 2.5 eV, which are in reasonable agreement with the experimental [40] and other DFT calculations [41]. The insulator feature is reproduced when an O vacancy

Table 1

Properties of the doped CeO₂ nanoparticles by both experiments and DFT numerical calculation.

Lattice	CeO ₂	La/CeO ₂	Nd/CeO ₂	Yb/CeO ₂
Average size (Å) by XRD	198	188	194	197
Lattice constant (Å) by XRD	5.41051	5.42264	5.41734	5.41750
Lattice constant (Å) by DFT	5.42751	5.43696	5.43151	5.42595
O vacancy formation energy (eV) by DFT	3.27	1.10	1.00	−1.26
Concentration of Ce ³⁺ by XPS	0.146	0.194	0.235	0.264

is introduced to the pristine CeO₂. Similar results are found for the doped system considered here. Particularly, the DOS is found to be almost unchanged for the La/CeO₂ with and without an O vacancy. Previous work indicated that the electrons that occupy the new gap states are exactly localized on two Ce cations neighboring the O vacancy, and make the two Ce⁴⁺ cations reduced to Ce³⁺ [23,42]. Since O vacancy is directly related to the formation of Ce³⁺, a lower O vacancy formation energy is indicative of favorable formation of Ce³⁺ in CeO₂. In general, the formation energy of an O vacancy (E_{vac}) can be calculated by

$$E_{vac} = E(\text{cell}_{vac}) + 1/2E(\text{O}_2) - E(\text{cell}) \quad (1)$$

where $E(\text{cell}_{vac})$ and $E(\text{cell})$ represent the energies of the supercells with and without an O vacancy, respectively, and $E(\text{O}_2)$ denotes the energy of the ground state of oxygen molecule. A positive E_{vac} value indicates energy is needed to create an O vacancy. From Table 1, the calculated E_{vac} for the pristine CeO₂ is 3.27 eV per vacancy, in line with other theoretical results [43]. For the La/CeO₂, Nd/CeO₂ and Yb/CeO₂, the E_{vac} is largely reduced to 1.10 eV, 1.00 eV and −1.26 eV, respectively. Notice that a positive to negative transition of the E_{vac} is predicted for the Yb/CeO₂, indicating that the creation of O vacancy is spontaneous under this condition. Such a large reduction in the O vacancy formation energy suggests that the lanthanide elements (La, Nd and Yb) could facilitate the formation of O vacancies in CeO₂ and also the associated change from Ce⁴⁺ to Ce³⁺ [44].

XPS data in Fig. 7(a–c) clearly show the existence of dopants in the RE/CeO₂ nanoparticles. Semi-quantitative calculation of Ce³⁺ content

in the RE/CeO₂ nanoparticles could be conducted by peak deconvolution of XPS spectra. The Ce 3d spectrum of CeO₂ is composed of spin-orbit split 3d_{3/2} at high binding energy and 3d_{5/2} at low binding energy. The spin-orbit split is ca.18.3 eV. Ten deconvolution peaks could be identified in the Ce 3d spectrum, which is in keeping with the literature [20]. The ten peaks are labeled as u, u₀, u', u'', u''' and v, v₀, v', v'', v''', as are schematically illustrated in Fig. 6(d). Deconvolution parameters used in this paper is shown in Table 2. By measuring the area of the each peak, the concentration of Ce³⁺ could be calculated according to the following equations:

$$C(\text{Ce}^{3+}) = A(\text{Ce}^{3+})/[A(\text{Ce}^{3+}) + A(\text{Ce}^{4+})] \quad (2)$$

$$A(\text{Ce}^{3+}) = A(u') + A(u_0) + A(v') + A(v_0) \quad (3)$$

$$A(\text{Ce}^{4+}) = A(u) + A(u'') + A(u''') + A(v) + A(v') + A(v'') \quad (4)$$

where C and A represent concentration and area, respectively. Therefore, the content of Ce³⁺ in CeO₂ is calculated based on the fraction of area (Ce³⁺) in the total area (Ce³⁺ and Ce⁴⁺). The calculated concentration of Ce³⁺ in all the CeO₂ samples is shown in Table 1. The concentration of Ce³⁺ in pristine CeO₂ is only 0.146. The concentration of Ce³⁺ significantly increases with the introduction of RE (RE = La, Nd and Yb) dopants for all the doped CeO₂ samples. The most obvious growth lies in the Yb/CeO₂ sample, with the content of Ce³⁺ up to 0.264. The calculation of Ce³⁺ content is in line with the DFT calculation of the O vacancy formation energy in CeO₂, as has been shown in Table 2. A higher content of Ce³⁺ cation leads to larger lattice strain and subsequent expansion of the lattice constant of ceria, because the crystal radius of Ce³⁺ is significantly larger than that of Ce⁴⁺, as has been aforementioned. Therefore, the lattice expansion after doping is under the effect of both the dopants (with large radii) and the increase of Ce³⁺ content in the RE/CeO₂ nanoparticles.

3.3. CMP of silica using RE/CeO₂ abrasive particles

Zeta potentials of abrasive particles and wafer surface determine the electrostatic interactions between them. If the abrasive particles and wafer surface are oppositely charged, the electrostatic attraction usually accelerates the polishing rate of the wafer material. Fig. 8 compares the Zeta potential of pristine CeO₂ nanoparticles and PECVD silica surface. Electrostatic repulsion takes place when the pH value of the slurry is higher than 6.5 or lower than 3.2. Conversely, electrostatic

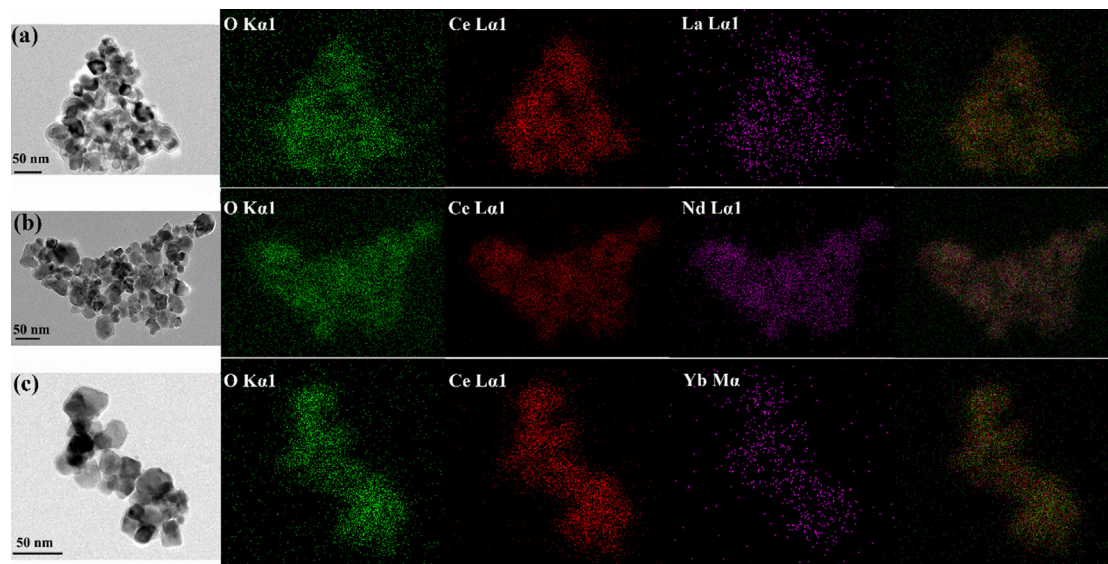


Fig. 4. The transmission electron microscopy (TEM) and energy disperse spectroscopy (EDS) mapping images of the as prepared RE/CeO₂ particles: (a) La/CeO₂; (b) Nd/CeO₂; (c) Yb/CeO₂. RE load is 5%.

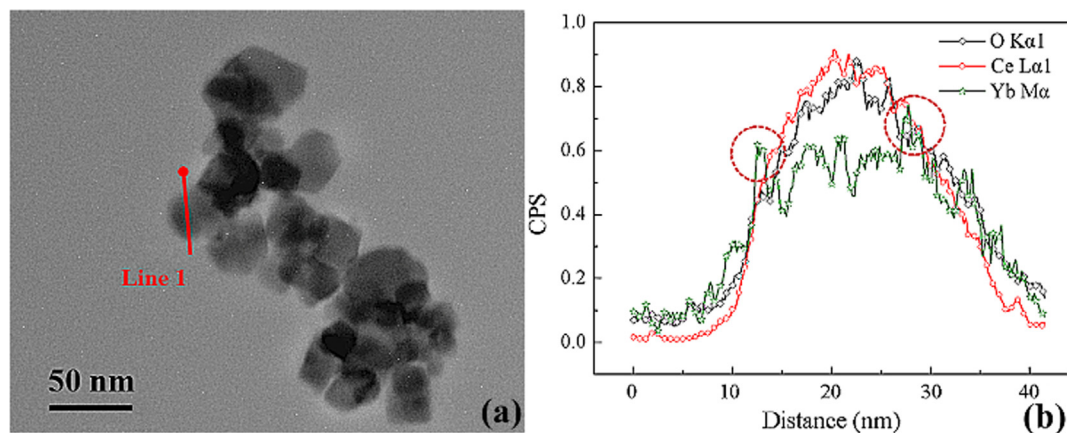


Fig. 5. (a) The transmission electron microscopy (TEM) image of Nd/CeO₂ nanoparticles and (b) the element distribution profile of Line 1 indicated in (a).

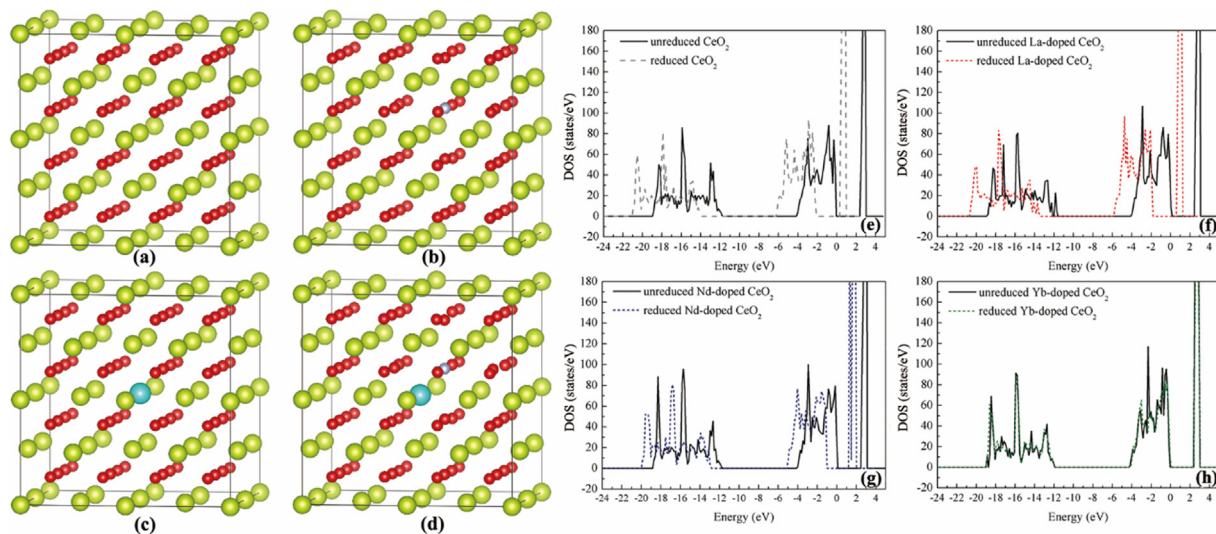


Fig. 6. Starting configurations for doped CeO₂: (a) CeO₂; (b) CeO₂ with one oxygen vacancy placed nearest neighbor to the dopant; (c) CeO₂ with one dopant; (d) CeO₂ with one dopant and one oxygen vacancy placed nearest neighbor to the dopant. Ce, O and dopant are marked as yellow, brown and blue, respectively. (d–h) the density of states (DOS) of CeO₂ including dopants and oxygen vacancy.

attraction occurs when the pH value is between 3.2 and 6.5.

This explains the reason why the MRR of silica is obviously lower when the pH value is 9.5, compared with that when the pH value is 5, the results of which are shown in the CMP experimental results in Fig. 9. Fig. 10 illustrates the MRR of silica during polishing with different CeO₂ as abrasive particles. Overall speaking, MRR of SiO₂ is higher in acidic slurries (at pH 5) than that in alkaline slurries (at pH 9.5), mainly due to the different electrostatic interactions between abrasive and the wafer surface. When RE/CeO₂ is used in acidic slurries, no enhancement of MRR of SiO₂ could be observed. On the contrary, a significantly improved MRR of SiO₂ is introduced when RE/CeO₂ is used in the alkaline slurries at pH 9.5. The doped CeO₂ as polishing abrasive particles could achieve an increase of SiO₂ removal rate at 20.9%, 29.6% and 4.3% for La/CeO₂, Nd/CeO₂ and Yb/CeO₂, respectively. Yb/CeO₂ shows the most increased Ce³⁺ content (0.363) compared with La/CeO₂ and Nd/CeO₂, but the promotion in the polishing rate of silica is not prominent (only 4.3%). Therefore, the chemical interaction between Ce³⁺ and dielectric surface is only one of the influencing factors during CMP, others such as electrostatic interactions and physical properties of abrasive particles should also be taken into account.

Surface topography after polishing is crucial to evaluate the CMP effect. The topography of SiO₂ wafer after CMP is shown in Fig. 10. Commercial CeO₂ abrasive particle (No. 2815) was used for

comparison. Results show that the surface roughness (Sa) of SiO₂ after CMP by using RE/CeO₂ nanoparticles is ca. 10 Å, which shows improvement compared with that of the No. 2815 commercial CeO₂ abrasive (Sa of ca. 14 Å). Therefore, the RE-doped CeO₂ nanoparticles (RE = La, Nd or Yb) exhibit improved properties when used as abrasive particles in alkaline slurry for the CMP of silica, with both the accelerated polishing rate and better surface quality after polishing.

4. Conclusions

To improve the CMP performance of CeO₂ as abrasive particles, Lanthanide metals (La, Nd and Yb) doped ceria nanoparticles were prepared by modified incipient impregnation method. Surface doping of CeO₂ nanoparticles could be achieved without affecting the original morphology as abrasive particle, which is proved by TEM/EDS analysis. XPS experiments and DFT numerical calculation indicate that the introduction of dopants (La, Nd and Yb) could facilitate the formation of oxygen vacancy and transition from Ce⁴⁺ to Ce³⁺ in CeO₂. The fraction of Ce³⁺ in the doped ceria is significantly increased, which is one of the decisive factors for improving the material removal rate of SiO₂ during polishing. The Ce³⁺ content in ceria increases from 0.146 to 0.194, 0.235, and 0.264 for the La/CeO₂, Nd/CeO₂ and Yb/CeO₂, respectively. At the same time, the polishing rate of silica in alkaline slurries is improved by 20.9%, 29.6% and 4.3% when La/CeO₂, Nd/CeO₂ and Yb/

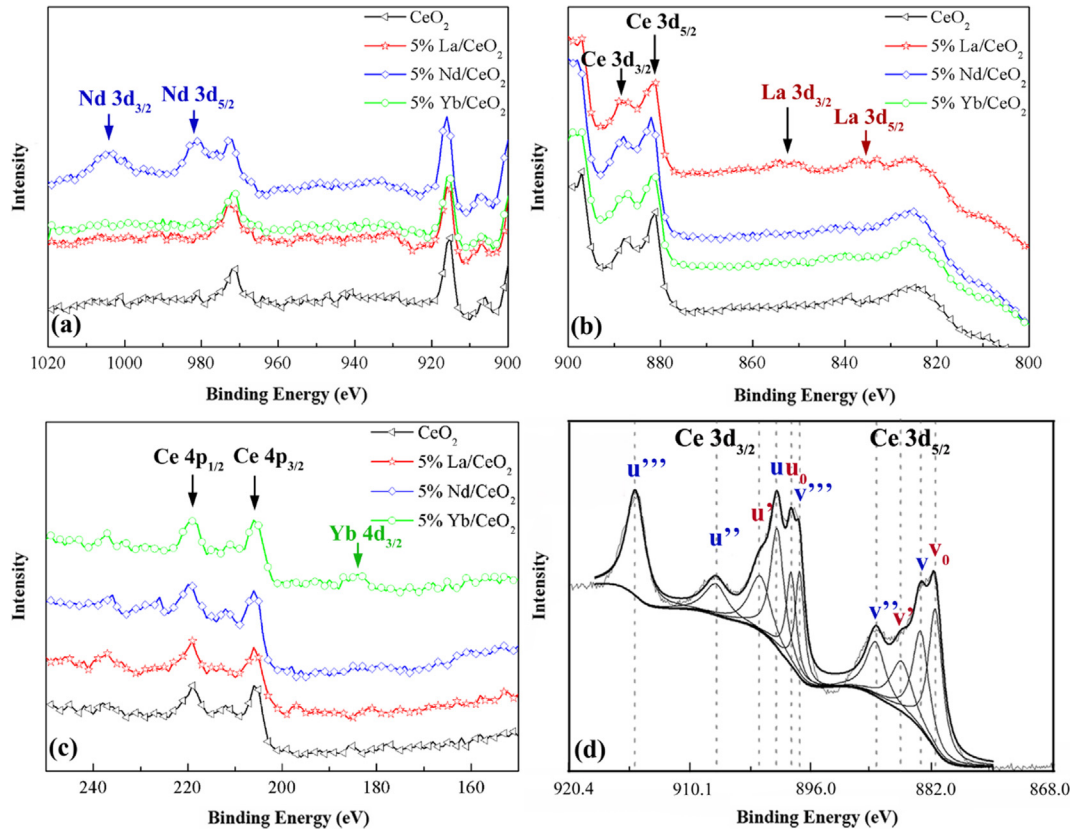


Fig. 7. X-ray photoelectron spectroscopy (XPS) results of CeO_2 particles: (a), (b) and (c) show different binding energy ranges; (d) an illustration of the $\text{Ce } 3d_{3/2}$ and $3d_{5/2}$ spin-orbit doublet spectrum and the peak deconvolution.

Table 2

Peak deconvolution parameters for the $\text{Ce } 3d$ X-ray photoelectron spectroscopy (XPS) spectrum in Fig. 7(d).

	Ce^{3+}				Ce^{4+}					
	v_0	v'	u_0	u'	v	v''	v'''	u	u''	u'''
Binding energy (eV)	800.9	884.9	899.6	903.3	882.1	888.5	897.9	900.6	907.2	916.2
FWHM (eV)	2.0	2.9	2.5	2.9	2.5	2.8	2.0	2.2	2.3	2.5

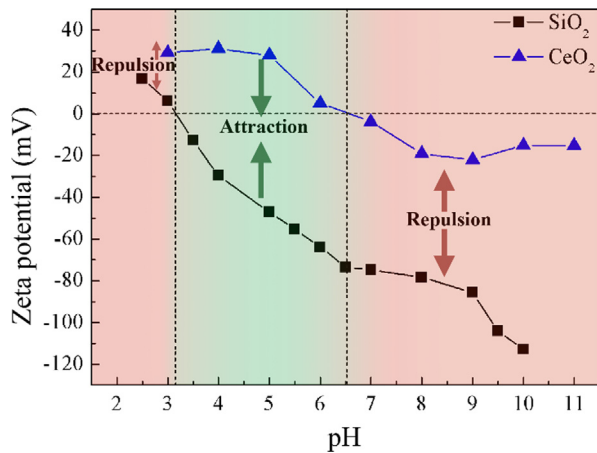


Fig. 8. Zeta potential of pristine CeO_2 nanoparticles and silica surface as a function of slurry pH values.

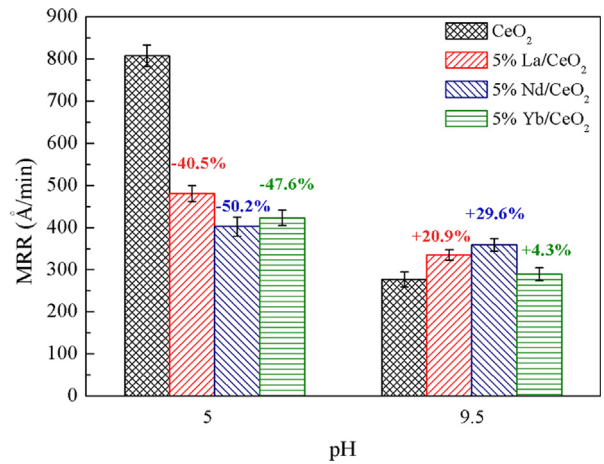


Fig. 9. The material removal rate (MRR) of silica dielectric during chemical mechanical polishing (CMP) by using different CeO_2 abrasive particles. The slurry contains 0.25 wt% abrasive particles.

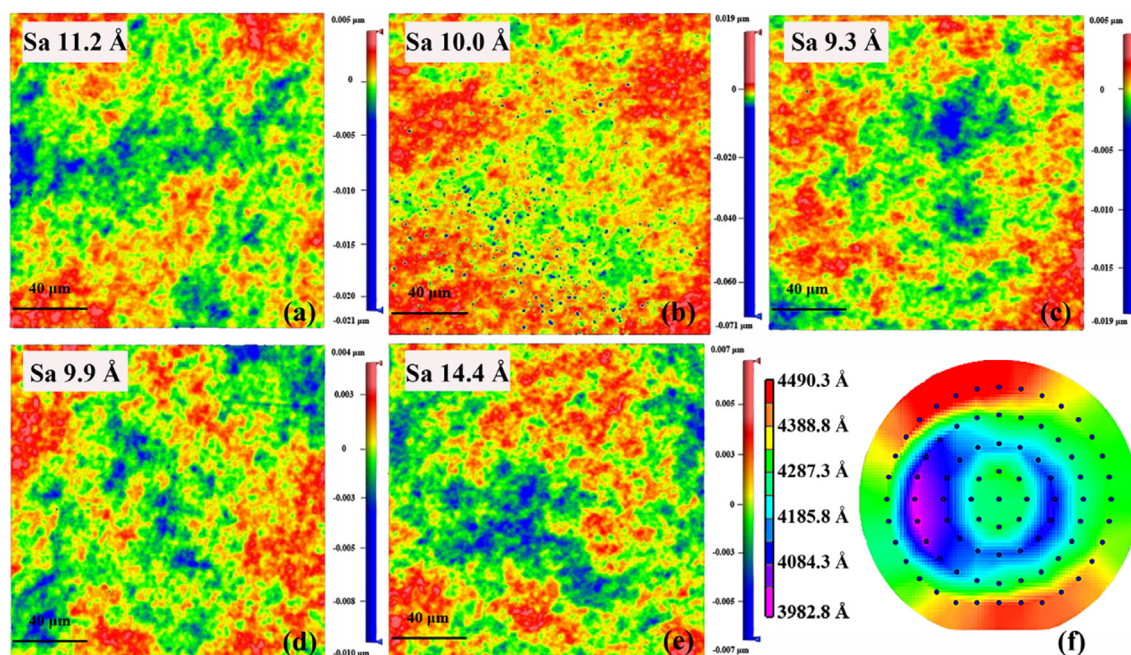


Fig. 10. Surface topography of silica dielectric after polishing by using different CeO₂ abrasive particles: (a) La/CeO₂; (b) Nd/CeO₂; (c) Yb/CeO₂; (d) pristine CeO₂; (e) commercial No. 1815 CeO₂. (f) Within wafer uniformity after polishing.

CeO₂ is used as abrasive particles during CMP. Based on overall consideration, Nd/CeO₂ is the most promising candidate among them as modified CeO₂ abrasive particles, with a increased content of Ce³⁺ of 0.235, improved SiO₂ polishing rate of silica at 29.6%, and a better surface quality after polishing (Sa = 9.3 Å).

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

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